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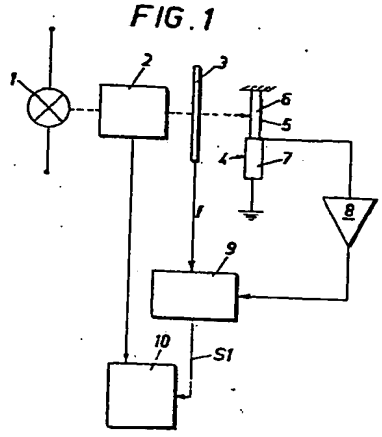
(54) **Photothermal measurement cell for study of light absorption by a sample substance.**

(57) A photothermal measurement cell for study of light absorption by a sample substance. The sample substance (5) is placed in contact with a temperature expansion element (6) of a solid material, for example quartz, glass, sapphire or the equivalent. The said element is arranged in contact with a mechanoelectric or mechanooptical transducer (7), for example a piezoelectric crystal. As the light is absorbed by the sample substance its temperature is raised, whereupon the temperature expansion element (6) expands and its mechanical motion is transformed to an electric signal by the transducer (7), whereupon the signal is amplified and registered for example by an X-Y recorder (10).

FIG. 1



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Photothermal measurement cell for study of light absorption by a sample substance

Background of the invention

The present invention is a photothermal measurement cell for study of light absorption by a sample substance which is illuminated by light with a modulated intensity and where the temperature increase proportional to the light absorption in the sample substance is arranged so as to be transformed into an electrical signal whose intensity is so arranged as to be detected by a registration apparatus.

One of the most important analysis methods for gases, liquids or solids is absorption spectroscopy. The whole optical range, from ultraviolet to long range infrared is used. Normally a measurement is performed by allowing a light beam to pass through a sample and then be referred to a reference beam. The difference in intensity between the two beams is measured and is a measure of the light absorption in the sample. This method has two weaknesses. The method is not applicable to measurement of very small light absorption, for example in measurement of small concentrations of foreign substances or in measurement of thin layers or surfaces. For very small absorption one must measure the difference between two almost equal light intensities, which is very difficult. The method further requires samples of good optical quality, that is, the samples must not scatter light. The method can therefore not be applied to powders, for example.

A way of circumventing these two disadvantages is to measure the signal which is proportional to the absorption in the sample directly instead of a signal which is proportional to the transmission. Such a signal is the sample temperature. When the light is absorbed in the sample a temperature increase is obtained which is proportional to the absorbed energy. The optical quality of the sample plays less of a roll here. Further very small absorptions can be measured if

the temperature measurement can be made sufficiently large.

In the American patent 3.948.345 a method is described which is called photoacoustic spectroscopy, in which the sample is contained in a gas-tight sample cell containing a small volume of air or other gas. As the sample is heated by illumination the air nearest the sample expands, which gives rise to a pressure change in the sample cell. This pressure change is registered by a microphone. The light beam is chopped at a low frequency (about 100 Hz) in an arrangement which alternatively lets the light pass or alternatively blocks its passage. The microphone signal is measured with a narrow band measurement system (phase locked detection) in order to achieve maximum sensitivity.

Commercial photoacoustic instruments have been available since 1977, but in limited quantities and the method has not been applied in industry to any great extent.

The purpose of the invention and its most important characteristics

The purpose of the present invention is to achieve a simplified photothermal measurement cell, with which one can measure the temperature increase of a sample which is illuminated. The application of the sample substance is by a simple means and the measurement cell can be used for analysis of both solids and fluids. The sensitivity should naturally be high.

This has been achieved by the sample substance being placed in contact with or alternatively itself being one or more temperature expansion elements of solid material, and by one or more mechanoelectric or mechanooptical transducers being in contact with one or some of the temperature expansion element's sides.

Description of the drawings

The invention will be described in more detail in the following with reference to two example embodiments shown in the attached figures.

Figure 1 is a schematic block diagram of a measurement system in which the measurement cell according to the invention is a part,
Figure 2 is a perspective view of an embodiment of the measurement cell according to the invention,
Figure 3 is a cross section through line III-III in figure 2,
Figure 4 is a modified embodiment of the measurement cell according to the invention, and
Figure 5 shows spectra taken with the measurement cell according to the invention.

Description of example embodiments of the invention

In figure 1 a lamp, for example a Xenon or halogen lamp, whose light is directed toward a monochromator 2, is designated by 1. The monochromator 2 is variable and thus gives a light beam with a certain desired wavelength, for example in the visible spectrum. One can also obtain a variation of the wavelength with time. A so called chopper 3 chops the light beam by alternately blocking the passage for the light beam or allowing its passage with a certain frequency f.

The wavelength separated and chopped light beam passes into a measurement cell 4 in which the sample 5 to be analyzed is placed. The sample 5, which can be a solid or a fluid, is placed in contact with an optically transparent temperature expansion element 6, for example a thin piece of glass quartz, sapphire or the equivalent. The requirements one has on the material in question are that itself shall have very little absorption in the wavelength region under consideration, that is shall have a measureable temperature expansion and that it shall be chemically inert to the samples under study.

As the light is absorbed by the sample 5 a temperature increase proportional to the absorbed energy is obtained. Only light absorbed within a certain distance from the temperature expansion element 6 contributes to the temperature rise in the temperature expansion element 6. This distance is known as the thermal diffusion length. As the thermal diffusion length is small for normal samples and for normal modulation frequencies, only a very small part of the hole sample volume is analysed. For water as a sample and for a modulation frequency of 100 Hz the thermal diffusion length is 0.002 cm. In the present setup, therefore, only 0,2% of the whole sample is analysed. Each light pulse from the chopper 3 gives rise to a temperature increase of the sample and each interval between the pulses allows cooling of the sample.

The temperature variations in the sample 5 give rise to an alternating expansion and contraction of the expansion element 6 which is arranged in contact with a mechanoelectric transducer 7, for example a piezoelectric crystal.

The mechanoelectric transducer 7 transforms the expansion and contraction motion of the expansion element to an electric signal, which is amplified by a preamplifier 8 and transmitted to a phase locked amplifier 9 in order that maximum sensitivity be obtained. The mechanical motion of the expansion element can also be detected by optical means, for example using an interferometer.

The output signal S_1 from the phase locked amplifier 9 corresponds to the light absorption of the sample 5 as it was detected by the mechanoelectric transducer 7. The output signal S_1 is registered on the Y axis of an X-Y registration instrument 10 and can be moved along the registration instrument's 10 X axis together with the monochromator's 2 wavelength variation, giving an absorption spectrum for the sample substance in the wavelength region under study. Of

course it is also possible to simply use a certain wavelength for the measurement when determining the content of a substance which one knows has an absorption maximum at a certain wavelength.

If one desires to have a normalized measurement in order to eliminate the effect of variations in the intensity of the lamp 1 at different wavelengths a reference measurement cell is arranged with for example a black expansion element 6. The output signal from the reference measurement cell is amplified in a preamplifier and transmitted to a phase locked amplifier in the same way as for the output signal from the measurement cell 4. The output signal S_2 from the phase locked amplifier is compared with the output signal S_1 and the divided value S_1/S_2 represents a normalized measurement value of the light absorption of the sample 5. The divided measurement value S_1/S_2 is registered by the X-Y registration instrument 10.

An example embodiment of the measurement 4 cell according to the invention will now be described in detail with reference to figures 2 and 3. The measurement cell 4 contains two housings 11 and 12 fixed against each other. Through the first housing 11 is an opening which forms the light passage. The expansion element 6, for example a thin piece of glass, quartz, sapphire or the equivalent, is mounted in the said opening 13 across it. The first housing 11 consists of two (screwed down) pieces fixed against each other, between which the expansion element 6 is fixed.

The expansion element 6 is placed with one side against a mechanoelectric transducer 7, for example a piezoelectric crystal, which is arranged in an enlarged part 14 of a volume in the second housing 12, which volume is arranged perpendicularly to the opening in the first housing 11. The transducer's 7 contact pressure against the expansion element 6 can be adjusted by a screw 16, which is threaded in the said volume 15. A plate 17 contacts the inside end of the

screw 16 on one side and has the opposite side against the transducer 17. Electrical contacts 18 are arranged from the transducer 7. Because the screw 16, the plate 17 and the transducer 7 are movable in the second housing's 12 volume 14, 15 expansion elements of different sizes can be placed in the measurement cell, for example in cases where the expansion element is also the sample substance, for example a piece of metal with oxide on its surface.

If the sample substance is for example a powder, a liquid, gel, colloid or similar substance it is placed directly on the whole surface of the expansion element 6. The amount of sample substance which is applied has little or no importance for the measurement result because it is only the temperature increase in the layer adjacent to the expansion element 6 of the sample substance which is detected and registered.

It is also possible to analyse several substances simultaneously by applying them on different parts of the expansion element's 6 surface and directing the light beam toward one of those parts at a time.

In certain cases, for example in process control, it can be desirable to carry out continuous registration of the light absorption of a sample substance, for example a powder, liquid, gel or their equivalent. The sample is then allowed to flow through the measurement cell 4 over the expansion element 6 with a certain speed. A measurement cell for this purpose is shown in figure 5 and contains a passage 19 through the first housing 11, which passage is placed across the opening 13. Tube connections are appropriately arranged at the inlet and outlet of the passage 19 in the measurement cell 4.

In cases where one desires to study how a chemical reaction changes the light absorption of the sample substance, for example in order to study the reaction speed of a chemical reaction, this is made possible by placing a substance, for

example an enzyme which reacts with the sample substance, in the measurement cell.

Of course it is possible to have two or more light passages each with its own expansion element 6 in the same measurement cell 4, which expansion elements 6 are in contact with a transducer 7. In this way one can study the difference in light absorption by two or more sample substances, when for example the light absorption in one of the sample substances can be changed because of a chemical reaction.

It is clear from the above description that the application area of the measurement cell according to the invention is large, and that it shows significiant advantages in regard to simplicity of construction and sample application compared to previously known methods and arrangements for study of light absorption by a sample substance.

The open cell makes sample changes simple. It can easily be built for a (continuous) flow of liquid through it. The fact that the cell is open makes it possible for example to continuously study chemical reactions in colloidal solutions through an addition of reagents.

As a proof of the measurement cell's excellent sensitivity one is referred to figure 5 which shows two spectra of red ink taken with the measurement cell under discussion. Spectrum I is for very dilute ink while spectrum II is for concentrated ink. The difference in the forms of the spectra is due to a saturation effect (spectrum II).

The invention is naturally not restricted to the example embodiments shown in the figures but can be varied within the limits of the claims.

Claims

1. Photothermal measurement cell for study of light absorption by a sample substance which is illuminated by light of a modulated intensity and where the temperature increase of the sample substance proportional to the light absorption is arranged to be transformed to an electrical signal whose intensity is arranged to be registered by a registration apparatus,
c h a r a c t e r i z e d b y
that the sample substance (5) is placed in contact with or alternatively consists of one or more temperature expansion elements (6) of solid material, and that one or more mechano-electric or mechanooptical transducers (7) are brought into contact with one or more of the sides of the temperature expansion element.

2. Photothermal measurement cell according to claim 1,
c h a r a c t e r i z e d b y
that the temperature expansion element (6) consists of a plate of a transparent chemically inert material such as quartz, glass, sapphire etc.

3.Photothermal measurement cell according to claims 1 or 2,
c h a r a c t e r i z e d b y
that the mechanoelectrical transducer consists of a piezo-electric material.

4. Photothermal measurement cell according to one or more of the previous claims,
c h a r a c t e r i z e d b y
that a part of the temperature expansion element (6) is treated with colored material in a way that is different from that of the remainder of the element, for example painted black.

5. Photothermal measurement cell according to one or more of the previous claims,
c h a r a c t e r i z e d b y
that the measurement cell shows a penetrating passage (19) for a sample substance, for example a powder, a liquid, gel, colloid or similar substance, which passage is arranged to extend over the temperature expansion element (6) which comprises a part of the wall of the passage.

6. Photothermal measurement cell according to one or more of the previous claims,
c h a r a c t e r i z e d b y
that the measurement cell (4) shows two or more temperature expansion elements (6) which are arranged in contact with mechanoelectric or mechanooptical transducers (7).

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FIG. 1

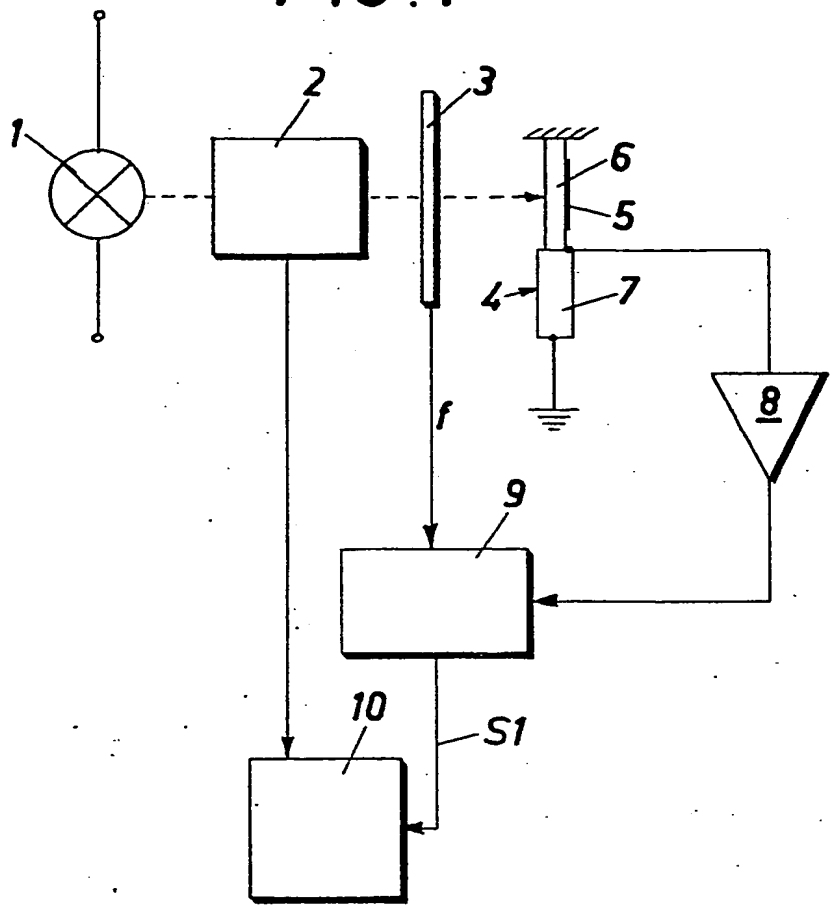

FIG. 2

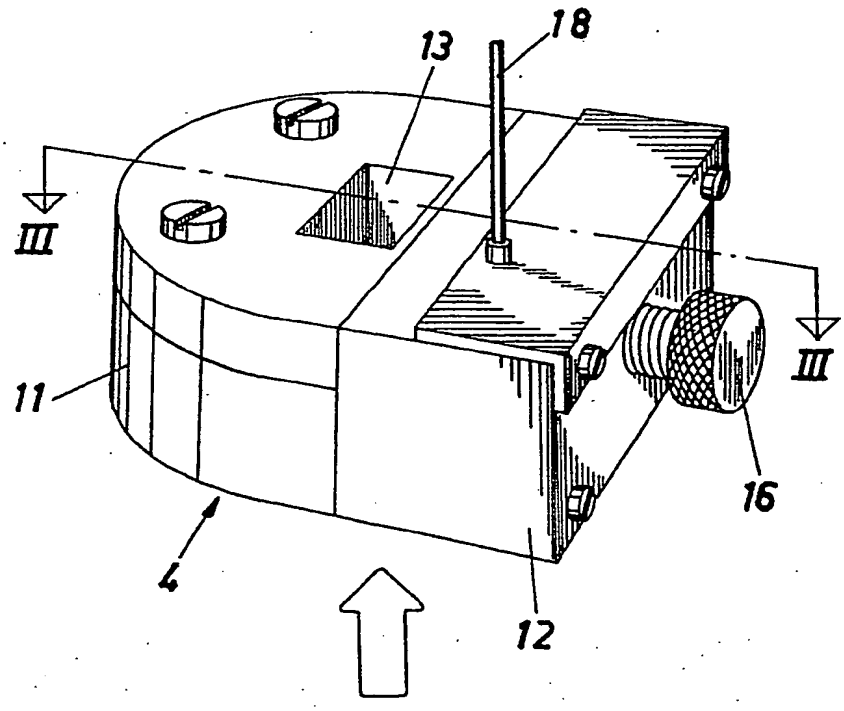

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FIG. 3

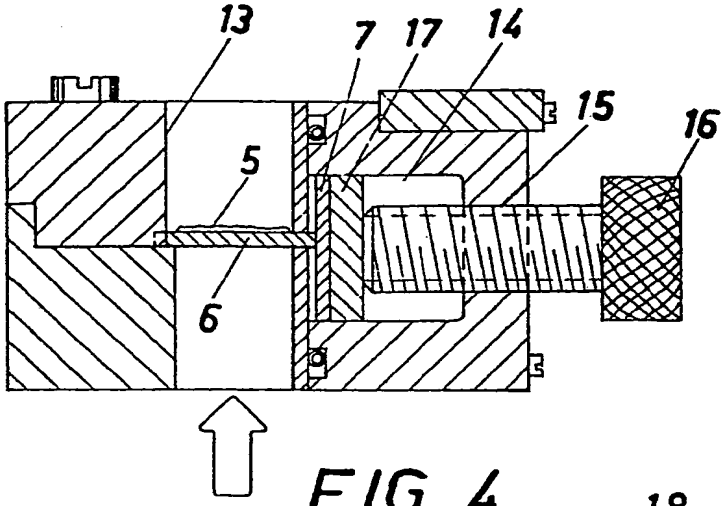

FIG. 4

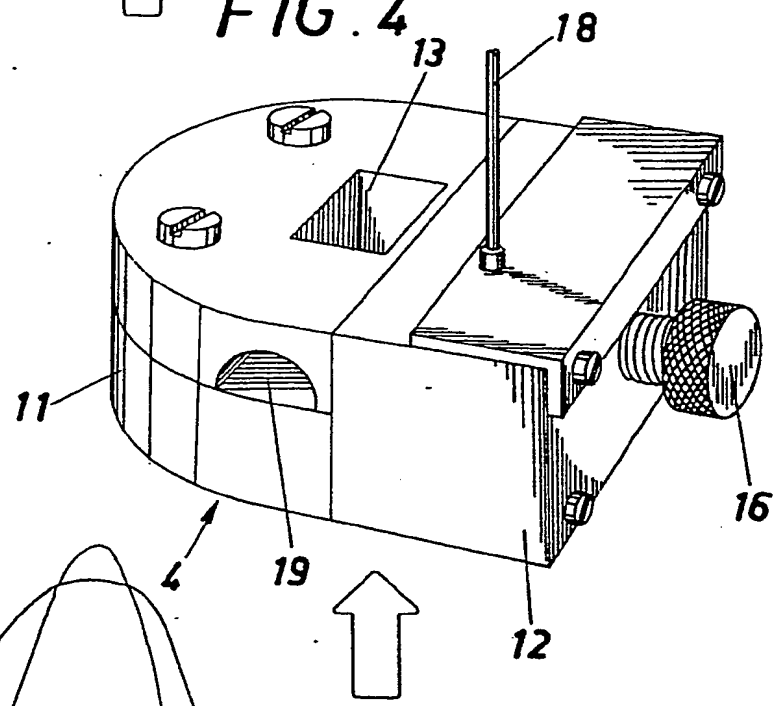

FIG. 5

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EUROPEAN SEARCH REPORT

Application number
EP 81 20 1077

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	APPLIED PHYSICS LETTERS, vol.35, no.11, December 1979 NEW YORK (US) A.C. TAM et al:"High-Resolution Optoacoustic Spectroscopy of Rare-Earth Oxide Powders" pages 843-845 * the whole document *	1-3
A	JOURNAL OF APPLIED PHYSICS, vol. 51, no.8, August 1980 NEW YORK (US) A. ROSENCWAIG et al.:"Photoacoustic Absorption Measurements of Optical Materials and Thin Films" pages 4361-4364 * pages 4361-4362; figures 1,2 *	1

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

G 01 N 29/00
21/59

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

G 01 N 29/00
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21/37

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	20-01-1982	BOEHM

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